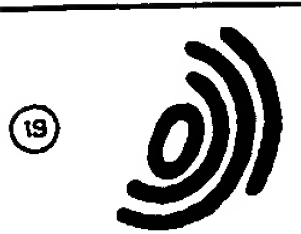


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EP-A- 0 172 724  
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US-A- 3 726 804

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## Description

The present invention is concerned with a process for preparing polymeric particles. More particularly, though not exclusively, the invention is concerned with a process for preparing an aqueous dispersion of water-insoluble core/shell particles.

In U.S.-A-3,891,577 a vesiculated polymer is prepared by converting to a solid polymer, a liquid medium containing dispersed therein particles of another polymer swollen by a liquid swellant, the liquid swellant then being at least partially removed from the dispersed polymer particle. The liquid medium may be converted to a solid by removal of solvent, e.g., from a solution of the solid polymer, or preferably, by polymerization of a monomer, comonomers, or an oligomer or a mixture of these. Optionally, a dissolved polymer may be present in the liquid to be polymerized. Solidification of the liquid in which these swollen particles are dispersed and removal of the swellant is then carried out to provide the vesiculated polymer, which may be in bulk form, as a film, or in the form of a coating applied to a substrate.

In another embodiment, US-A-3,891,577 teaches that the dispersion of swollen polymer in the liquid medium may itself be dispersed in a further liquid in which it is insoluble. The further liquid is referred to as the suspending liquid. Solidification of the medium is then carried out and after separation of the granules formed from the suspending liquid, liquid swellant may be removed from the swollen polymer to provide vesiculated polymer in granular form. Alternatively, when, for example, the vesiculated granules are to be used in a coating composition with which the suspending liquid is compatible, the granules formed by solidification of the medium may be incorporated into the composition as a slurry in at least part of the suspending liquid. On applying the composition to a substrate, formation of a coating film and removal of swellant from the swollen dispersed polymer to form the vesicles within the granule then take place concurrently.

U.S.-A-3,870,099 discloses the preparation of sequential acrylic polymers containing 0.5-2.5% of an  $\alpha$ ,  $\beta$ -unsaturated carboxylic acid. The bulk of the acid is introduced in the early part of the polymerization.

U.S.-A-4,427,836 discloses the production and use of water-insoluble particulate heteropolymers made by sequential emulsion polymerization in dispersed particles of which a core of a polymeric acid is at least partially encased in a sheath polymer that is permeable to a volatile base, such as ammonia or an organic amine, adapted to cause swelling of the core by neutralization. The sheath is not permeable to permanent, non-volatile bases such as sodium hydroxide. The aqueous dispersion of the acid-containing core/sheath particles is useful in making water-based coating composition wherein it may serve as an opacifying agent when the volatile base is used to at least partially neutralize the heteropolymer, microvoids being formed in cores of the swollen particles and the film during the drying. Although the core may be made in a single stage of the sequential polymerization and the sheath may be the product of the single sequential stage following the core stage, the making of the core component may involve a plurality of steps in sequence followed by the making of the sheath which also may involve a series of sequential steps. Thus the first stage of the emulsion polymerization in the process of US-A-4,427,836 may be the preparation of a seed polymer containing small dispersed polymer particles insoluble in the aqueous emulsion polymerization medium. This seed polymer, which may or may not contain any acid component, provides particles of minute size which form the nuclei on which the core polymer of acid monomer, with or without nonionic comonomers, is formed. The polymer particles of this invention are prepared by aqueous emulsion polymerization, which requires a water-soluble free radical initiator, or a mixture of such an initiator with a water-soluble reducing agent to form a redox system. In a preferred embodiment a seed polymer is used along with a low level of core stage emulsifier. By carrying out the emulsion polymerization while maintaining low levels of emulsifier, the subsequent stages of polymer formation deposit the most recently formed polymer on the existing dispersed polymer particles resulting from the preceding step or stage. If the amount of emulsifier is kept below the amount corresponding to the critical micelle concentration (CMC) for a particular monomer system, a preferred unimodal product results. While the CMC may be exceeded somewhat without the formation of an objectionable or excessive number of dispersed micelles or particles, it is preferred that the number of micelles during the various stages of polymerization be controlled so that the deposition of the subsequently formed polymer in each stage occurs upon the dispersed micelles or particles formed in the previous stages.

U.S.-A-4,469,825 discloses core/sheath polymer particles wherein the core monomer system requires an amine group-containing comonomer which comprises at least 5% by weight of the core monomer system.

U.S.-A-4,468,498 discloses a process for making an aqueous dispersion of core/sheath polymers in which the core contains sufficient acid groups to render the core swellable by neutralization with a volatile

base to at least twice its volume and wherein the sheath is permeable to the base.

U.S.-A-4,049,604 discloses aqueous dispersions of normally solid, organic polymeric particles that are prepared by (1) dispersing an oil phase containing at least one emulsion polymerizable monomer such as styrene in an aqueous phase containing a stabilizing emulsifier such as sodium dodecylbenzene sulfonate and a copolymer of a sulfo ester of an alpha, beta-ethylenically unsaturated carboxylic acid, such as 2-sulfoethyl methacrylate, and butyl acrylate and (2) subjecting the dispersion to emulsion polymerization. Microspheres having liquid centers and seamless rigid walls of the normally solid, organic polymer are prepared according to this method except that the starting oil phase also contains a nonpolymerizable, water-insoluble liquid such as hexane. The polymers of sulfo esters of alpha, beta-ethylenically unsaturated carboxylic acids serve as coalescence aids. The diameter of the resulting microspheres is inversely related to the concentration of the polymer of sulfo ester employed (operable range: 0.2 to 2.0 weight percent). Microspheres by this process have an average diameter of from about 0.5 to about 3 microns, when the amount of sulfoester employed is at the upper end of the acceptable range. Microspheres of this size are suspensions and not dispersions, they will settle out of the aqueous medium on standing.

U.S.-A-4,336,173 discloses a process for preparing an aqueous emulsion or dispersion of a partly water-soluble material and optionally further conversion of the prepared dispersion or emulsion to a polymer dispersion when the partly water-soluble material is a polymerization monomer. In the first step a dispersion of polymer particles is prepared containing one or more materials having very low solubility in water, then in a second step there is added the partly water-soluble material which diffuses into the particles from the first step, and then, if the partly water-soluble material is a polymerizable monomer, polymerization may be affected. By using a seed consisting of a polymer and essentially water-insoluble material, the seed particles will be capable of absorbing much greater amounts of monomer, it often being possible to add all the monomer in one step, and the amount of seed employed may be greatly reduced, in comparison with conventional emulsion seeded polymerization. In the conventional process, the seed particles consists of polymer molecules which are capable of absorbing only one to four times their own volume in polymerizable monomer; however, the Ugelstad seed can absorb much greater amounts of monomer. Thus the tendency to form a second mode of unseeded polymer particles during the polymerization of the monomer swollen seeds is reduced. Either a water-soluble initiator such as potassium persulfate or hydrogen peroxide or an oil-soluble initiator such as lauryl peroxide may be employed.

U.S.-A-4,113,687 discloses a process for preparing a latex by efficiently homogenizing an aqueous mixture containing an emulsifier and a water-insoluble solvent for the monomer to be polymerized, adding monomer and, if desired, further water to the homogenized mixture and also water-soluble polymerization initiator. Instead of a water-soluble initiator, an oil soluble initiator may be used provided it has sufficient solubility diffused through the aqueous phase into the drops of water insoluble solvent and monomer.

Microencapsulation methods and the properties of the resulting microcapsulates are reviewed by T. Kondo in Surface and Colloid Science, Volume 10 (Plenum Press, New York 1978) pp. 1-41. Microencapsulation is also reviewed by R. E. Sparks in Kirk-Othmer, Encyclopedia of Chemical Technology, Volume 15 (3rd Edition) pp. 470-492. Microencapsulation of water immiscible materials, such as aqueous dispersions of pesticides and herbicides, is reviewed in U.S.-A-4,417,916 and U.S.-A-4,280,833, in which an improved microencapsulation process employing lignin sulfonate emulsifier and the reaction of poly-methylene polyphenylisocyanate and a polyfunctional amine is taught. U.S.-A-4,360,376 teaches an interfacial polycondensation method of microencapsulating trifluralin, a pre-emergent herbicide. U.S.-A-4,155,741 discloses a stable suspension-buffer system for aqueous suspensions of polyurea-microencapsulated materials, including herbicides and insecticides, which can be obtained by using aluminum hydroxide or ferric hydroxide as suspending agent, thereby preventing separation and caking in flowable microcapsule formulations.

It is an object of the present invention to provide, amongst others, a process for producing aqueous dispersions of polymeric core/shell particles prepared by sequential microsuspension polymerization having a core containing a blend of hydrophilic and hydrophobic materials.

In accordance with the present invention a process for preparing an aqueous dispersion of water-insoluble core/shell particles comprises

(a) preparing core emulsion by emulsifying in water at high shear a mixture comprising

(1) at least one hydrophobic solvent and/or organic target material

(2) at least one hydrophilic solvent,

(3) initial monomer comprising at least two polymerizable mono-ethylenically unsaturated compounds wherein said initial monomer includes from about 2 to 4% by weight, based on the total weight of said initial monomer of alpha, beta-ethylenically unsaturated carboxylic acid monomer,

(4) anionic surfactant

- (5) water-insoluble emulsion stabilizer, and  
 (6) water-insoluble thermal polymerization initiator, wherein said hydrophobic solvent and said hydrophilic solvent are non-solvents for a polymer prepared by polymerizing said initial monomer,  
 (b) heating said core emulsion to polymerize said initial monomer, thereby forming core particles,  
 5 (c) adding at least one base selected from ammonia and the organic amines thereby neutralizing polymerized carboxylic acid and forming core/shell particles, and optionally  
 (d) adding additional monomer whereby said additional monomer is polymerized on or in the previously formed said core/shell particles.

Practice of the invention may advantageously provide particles which are smaller in size than typical  
 10 particles produced by previously mentioned techniques and also the distribution of particle sizes may be more uniform. These particles may advantageously be useful in opacifying film formed by aqueous coating compositions through microvoid formation. This invention may also advantageously provide a process for microencapsulation of organic target materials in an aqueous dispersion of water-insoluble core/shell particles; because an aqueous medium is employed rather than an organic solvent for the preparation of the  
 15 microcapsule walls, the aqueous dispersions of microencapsulated target materials may be advantageously used directly in many applications, such as in preparing for agricultural use aqueous tank mixes of encapsulated pesticides and non-encapsulated fertilizer.

It is believed that neutralization of the carboxylic acid induces polymer carrying carboxylic acid functionality to migrate to the interface between the aqueous medium and the core particles, creating a  
 20 core/shell structure within the particles. However, the present invention is in no way limited by this explanation.

Where additional monomer is polymerized on or in the previously formed shell of the core/shell particles, the polymerization of the additional monomer may be initiated by residual water-insoluble thermal polymerization initiator within the already formed core/shell particles. In an alternative embodiment,  
 25 additional polymerization initiator may be added to the aqueous dispersion of core particles prior to the addition of the additional monomer. The additional polymerization initiator may also be added concurrently with or subsequently to the addition of the additional monomer. The additional polymerization initiator may be water insoluble, slightly water soluble or water soluble. When it is desired to avoid or minimize the formation of a second mode of polymer particles, polymerization of the additional monomer in the absence  
 30 of additional polymerization initiator is preferred. It is preferred that the additional monomer composition be chosen so that additional monomer when polymerized forms a shell upon the pre-existing core particles. Examples of additional polymerization initiators which may be employed include polymerization initiators of the free radical type, such as ammonium or potassium persulfate, which may be used alone or as the oxidizing component of a redox system, which also includes a reducing component such as potassium  
 35 metabisulfite, sodium thiosulfate or sodium formaldehyde sulfoxylate. The reducing component is frequently referred to as an accelerator. The initiator and accelerator, commonly referred to as catalyst, catalyst system or redox system, may be used in proportion from 0.01% to 3% each, based on the weight of monomers to be copolymerized. Examples of redox catalyst systems include t-butyl hydroperoxide/sodium formaldehyde sulfoxylate/Fe(II), and ammonium persulfate/sodium bisulfite/sodium hydrosulfite/Fe(II). The  
 40 polymerization temperature may be from room temperature to 90° C, and may be optimized for the catalyst system employed, as is conventional.

Chain transfer agents including mercaptans, polymercaptans and polyhalogen compounds are sometimes desirable in the polymerization mixtures to moderate polymer molecular weight. Examples of chain transfer agents which may be used included long chain alkyl mercaptans such as t-dodecyl mercaptans,  
 45 alcohols such as isopropanol, isobutanol, lauryl alcohol or t-octyl alcohol, carbon tetrachloride, tetrachloroethylene and trichlorobromoethane. Generally from 0 to 3% by weight, based on the weight of the monomer mixture, may be used.

If desired, the addition and polymerization of the additional monomer may be omitted, provided that the initial monomer is selected to yield polymer preferably having a calculated glass transition temperature ( $T_g$ )  
 50 greater than 70° C. Even when additional monomer is employed and is polymerized on core/shell particles, it is preferred that the core/shell particle polymer have a calculated  $T_g$  greater than 70° C. The  $T_g$  of a polymer with a specific monomer composition is determinable in a known manner either experimentally or by calculation. The method of calculating the  $T_g$  based upon the  $T_g$  of homopolymers of individual monomers is described by Fox, Bull. Am. Physics Soc. 1,3, pg. 123 (1956). Monomers may be selected to  
 55 obtain the appropriate  $T_g$  through use of the "Rohm and Haas Acrylic Glass Transition Temperature Analyzer", Publication CM-24 L/cb of Rohm and Haas Company, Philadelphia, PA. Examples of initial monomers which when polymerized will yield core polymer having a calculated  $T_g$  greater than 70° C are methyl methacrylate, styrene, and mixtures thereof.



It is preferred that the initial monomer be mono-alpha, beta-ethylenically unsaturated and preferably comprises at least 80% by weight, based on the weight of initial monomer, of monomer selected from methyl methacrylate, styrene, and mixtures thereof. Initial monomer comprising at least 50% by weight methyl methacrylate is especially preferred.

5 Examples of nonionic monoethylenically unsaturated monomers which may be employed in preparing the core/shell particle includes styrene, vinyl toluene, ethylene, vinyl acetate, vinyl chloride, vinylidene chloride, acrylonitrile, (meth)acrylamide, various (C<sub>1</sub>-C<sub>20</sub>) alkyl or (C<sub>3</sub>-C<sub>20</sub>) alkenyl esters of (meth)acrylic acid; for example, methyl methacrylate, methyl acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, benzyl (meth)acrylate, lauryl (meth)acrylate, oleo (meth)acrylates, palmityl (meth)acrylate, and stearyl (meth)acrylate. The expression (meth)acrylic acid is intended to serve as a generic  
10 expression embracing both acrylic and methacrylic acid. Similarly, the expression (meth)acrylate is intended as a generic expressions embracing both acrylic acid and methacrylic acid esters.

Examples of alpha, beta-ethylenically unsaturated carboxylic acid monomer which may be used to prepare the core/shell particles include acid monomers such as methacrylic acid, beta-acryloxypropionic acid, mixtures of beta-acryloxypropionic acid and higher oligomers of acrylic acid, methacryloxypropionic acid, itaconic acid, citraconic acid, crotonic acid, maleic acid or maleic anhydride, fumaric acid, monomethyl maleate, monomethyl fumarate and monomethyl itaconic, and mixtures thereof and mixtures of methacrylic and acrylic acids. The preferred acid monomers that may be employed in preparing the core particles of the present invention are methacrylic acid and mixtures of acrylic acid and methacrylic acid, especially  
15 preferred is methacrylic acid. It is preferred that the methacrylic acid comprise from 2 1/4 to 3% by weight, based on the total weight of initial monomer, of the initial monomer. Other preferred acid monomers that may be used include acryloxypropionic acid, and mixtures of acryloxypropionic acid and the higher oligomers of acrylic acid.

It is preferred that the initial monomer used to prepare the core/shell particles comprise up to 10% by weight, based on the total weight of initial monomer, of monomer selected from the group consisting of  
25 ethyl acrylate, acrylonitrile and mixtures thereof. Ethyl acrylate is especially preferred. When ethyl acrylate is employed, it is preferred that 5% by weight, based on the total weight of initial monomer, be used.

The hydrophobic solvent used in preparing the core particle is preferably selected from the acyclic paraffinic hydrocarbons, mixtures of the acyclic paraffinic hydrocarbons and cyclic paraffinic hydrocarbons  
30 and mixtures of acyclic paraffinic hydrocarbons, cyclic paraffinic hydrocarbons and aromatic hydrocarbons wherein the mixtures contain no more than 10% by weight, based on the total weight of the mixture, of aromatic hydrocarbons. Examples of hydrophobic solvents which may be employed include mineral spirits, petroleum spirits, ligroin, VM&P naphtha (varnish maker's and painter's naphtha), refined solvent naphtha, solvent naphtha, petroleum and petroleum benzin.

It is preferred that the 50% distillation temperature of the hydrophobic solvent be from 150° C to 200° C. It is especially preferred that a hydrophobic solvent with a 50% distillation temperature of from 160° C to 180° C be employed in the process of preparing the core particles. It is also preferred that the hydrophobic solvent be a mixture of acyclic paraffinic hydrocarbons and cyclic paraffinic hydrocarbons wherein the cyclic paraffinic hydrocarbons comprise no more than 5% by weight of the mixture.  
35

When the hydrophilic solvent is a hydroxyl compound, it is preferred that the proportion of hydrophilic solvent to hydrophobic solvent be chosen so that there are from 0.28 to 0.42 moles of hydroxyl functionality per 100 gms of hydrophilic/hydrophobic solvent blend. It is especially preferred that the proportion of hydrophilic to hydrophobic solvent be chosen to give 0.34 moles of hydroxyl functionality per 100 gms of solvent blend.  
40

The hydrophilic solvent employed in preparing the core particle is preferably selected from the isomers of butanol, pentanol, hexanol, and methyl isobutyl carbitol and mixtures thereof.  
45

The weight ratio of hydrophilic to hydrophobic solvent is preferably from 1:3 to 9:11, especially when pentanol is chosen as the hydrophilic solvent, and a ratio of 3:7 is especially preferred. When butanol is selected as hydrophilic solvent, a ratio of hydrophilic to hydrophobic solvent of 1:3 is especially preferred.  
50 When hexanol is chosen as hydrophilic solvent, a weight ratio of hydrophilic to hydrophobic solvent of 3.5:6.5 is especially preferred.

As anionic surfactant such as an alkali metal salt of a di(C<sub>7</sub>-C<sub>25</sub>)alkylsulfosuccinates or of an alkyl aryl sulfonate, is employed as an aid in preparing the initial dispersion of initial monomer, solvent mixture (including organic target material, if desired), and emulsion stabilizer.

55 Examples of suitable anionic dispersing agents include, for example, the higher fatty alcohol sulfates, such as sodium lauryl sulfate; alkylaryl sulfonates such as sodium or potassium isopropylbenzene sulfonates or isopropyl naphthalene sulfonates; alkali metal higher alkyl sulfosuccinates, such as sodium octyl sulfosuccinate, sodium N-methyl, N-palmitoyltaurate or sodium oleyl isothionate; and alkali metal salts of

alkylaryl polyethoxyethanol sulfates, sulfonates or phosphates, such as sodium *tert*-octylphenoxypolyethoxyethyl sulfates and nonyl phenoxypolyethoxy ethyl phosphates, either having 1 to 7 oxyethylene units. An example of a preferred alkali metal salt dioctylsulfosuccinate is sodium dioctyl sulfosuccinate. An example of a preferred alkylbenzene sulfonate is sodium dodecylbenzene sulfonate. It is preferred that the anionic surfactant comprise from 0.2 to 0.8% by weight of the organic phase of the core emulsion. It is especially preferred that the anionic surfactant comprise from 0.3 to 0.5% by weight of the organic phase of the core emulsion.

The water-insoluble emulsion stabilizer may be selected from organic compounds having a molecular weight of no more than 500 and a water solubility of no more than  $10^{-4}$  gms per liter. The water-insoluble emulsion stabilizer is preferably selected from the di(C<sub>4</sub>-C<sub>10</sub>)alkyl phthalates, dibutoxyethyl phthalate, *n*-butyl benzyl phthalate, dimethylcyclohexyl phthalate, dicyclohexyl phthalate, diphenyl phthalate, dipropeneglycol dibenzoate, diethyleneglycol dibenzoate, triethyleneglycol di-(2-ethylbutyrate), di-(2-ethylhexyl) adipate, di-isooctylazelate, di-(2-ethylhexyl)azelate, di-*n*-butyl sebacate, 1-chlorododecane, hexadecane, and mixtures thereof. An especially preferred water-insoluble emulsion stabilizer is di(2-ethylhexyl)phthalate (a/k/a dioctyl phthalate). It is preferred that the water-insoluble emulsion stabilizer comprise at least 0.25% by weight of the organic phase of the core emulsion. It is especially preferred that the water-insoluble emulsion stabilizer comprise from 2.5 to 4% by weight of the organic phase of the core emulsion.

The core emulsion contains a water-insoluble thermal polymerization initiator such as lauryl peroxide. The ratio of the weight of the water-insoluble thermal polymerization initiator to the total weight of initial monomer employed in preparing the core emulsion is preferably from 0.1:100 to 5:100. It is more preferred that the ratio of the weight of the water-insoluble thermal polymerization initiator to the total weight of the initial monomer be from 2.5:100 to 4:100.

The core emulsion is prepared by adding the solvent blend, initial monomer, emulsion stabilizer, anionic surfactant and water-insoluble initiator to water and subjecting the mixture to high mechanical shearing forces. The shear force may be applied mechanically as by use of a high shear mechanical disperser such as a Waring Blender (Waring is a trademark of Dynamic Corp. of America) or high speed impeller as are commonly used in coatings manufacture. Alternatively, the high shear dispersion may be accomplished ultrasonically. The average particle size and particle size distribution of the core emulsion is believed to depend upon the magnitude and duration of the shearing forces applied.

In addition, the particle size distribution is believed to depend on the nature and relative amount of anionic surfactant used, the nature and amounts of the solvents employed and the nature and relative amounts of the monomers to be copolymerized.

In view of these variable parameters a shear is therefore to be considered high if it is sufficient to form particles having the desired particle size and distribution.

It is preferred that the average particle size of the core emulsion after dispersion be from .22 to .35 micrometers as determined by photon correlation spectroscopy, particularly when the polymerised dispersion is to ultimately be used to impart opacity. Light scattering techniques such as photon correlation spectroscopy measure the Z-average particle size. It is especially preferred that the average particle size of the core emulsion after dispersion be from .27 to .32 micrometers, especially when the polymerized dispersion resulting from the core emulsion is to be used to impart opacity, as in coating compositions. Preferably the core/shell particles have a polydispersity index of from 1.5 to 5.

After the core emulsion has been formed, it is heated to activate the thermal water-insoluble polymerization initiator. The optimum polymerization temperature depends upon the thermal initiator used to effect the polymerization. When lauryl peroxide is employed the core emulsion is preferably heated to a temperature of from 86 to 89°C. Because the initial monomer and hydrophobic/hydrophilic solvent blend are chosen so that the polymer is formed from the initial monomers insoluble in the solvent blend, it is believed that the polymer forms a separate phase within the core emulsion when the initial monomer is polymerized. After polymerization of the initial monomer, the copolymerized residues of the acid monomer are neutralized by addition of a base selected from ammonia and an organic amine. Ammonia is preferred to effect the neutralization.

Subsequent to the neutralization of the polymerized carboxylic acid, additional monomer may be added to the core/shell particles. It is preferred that the additional monomer be selected to yield polymer having a calculated glass transition temperature greater than 70°C and preferably greater than 80°C. Any of the non-carboxylic acid monomers useful in preparing the core polymer may be employed as additional monomer. Thus, for example, ethyl acrylate, butyl acrylate, methyl methacrylate, styrene, and acrylonitrile may be employed. Mixtures of ethylenically unsaturated monomers, such as methyl methacrylate, butyl acrylate, and styrene mixtures may be used. Methyl methacrylate is preferred. It is especially preferred that the additional monomer comprise at least about 80% by weight, based on the total weight of the additional

monomer, of methyl methacrylate.

The additional monomer may also comprise at least one multi-alpha, beta-ethylenically unsaturated monomer. It is preferred that when such multi-alpha, beta-ethylenically unsaturated monomer is employed it comprise no more than 5% by weight of the total additional monomer. Preferred multi-alpha, beta-ethylenically unsaturated monomers useful as additional monomer are allyl (meth)acrylate, tripropyleneglycol di(meth)acrylate, diethyleneglycol di(meth)acrylate, ethyleneglycol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,3-butyleneglycol di(meth)acrylate, diallyl phthalate, trimethylolpropane tri(meth)acrylate, and divinylbenzene. Especially preferred multi-alpha, beta-ethylenically unsaturated monomers are allyl methacrylate, diallyl phthalate, and trimethylolpropane trimethacrylate.

It is preferred that the weight ratio of solvent blend (that is hydrophilic solvent and/or organic target material plus hydrophobic solvents) to initial monomer be from 1:0.8 to 1:3. It is especially preferred that the ratio of solvent blend to initial monomer be 1:1.3. It is preferred that the weight ratio of initial monomer to additional monomer be from 0.9 to 1.5. It is especially preferred that the weight ratio of initial monomer to additional monomer be 1.3:1.

The core/shell particles prepared by the process of the present invention are useful as opacifying agents in coatings compositions. Drying compositions which contain aqueous dispersions of these core/shell particles is believed to cause the formation of single individual voids within the core/shell particles which contribute to the opacity of the dried compositions containing the core/shell particles. When the core/shell particles of the present invention are used as opacifying agents, the amount of polymer deposited to form the shell polymer is generally such so as to provide an overall particle size of the core/shell particle of from 0.35 to 0.55 micrometers, preferably from about 0.42 to 0.48 micrometers, and a polydispersity index of from about 1.5 to 5.

The core/shell particles of the present invention are useful for aqueous coating and impregnating compositions such as those of U.S.-A-2,795,564, as opacifying agents and such compositions either as a supplement to, or replacement of, pigmentary matter and/or extenders therefor. For these purposes the aqueous dispersions of the core/shell polymer may be added directly to the coating and or impregnating compositions. Alternatively, the core/shell polymers may be isolated from the dispersions, by filtration or decantation, and then the organic solvent blend may be removed as by drying or volatilization, under conditions such that microvoids are formed and retained in the individual particles or granules, the latter being more or less free flowing in character so that they can be packaged, shipped or stored before use. The dry powder thus obtained can also be used in coatings based on organic solvents provided that the shell component of the core/shell particles is not soluble in the organic solvent.

Besides being useful in water-based paints based on vinyl or acrylic polymer lattices or aqueous solutions of vinyl or acrylate polymers, to replace all or part of opacifying pigments heretofore used, especially titanium dioxide, microvoid containing core/shell particles polymers of the present invention may be used for similar purposes in other coating systems, including resin formaldehyde condensation products of thermosetting type, such as phenoplast and aminoplast, including urea formaldehyde, and melamine formaldehyde, and other condensates, for example, water dispersible alkyd resins.

An opacified composition adapted for coating and/or impregnating a surface may comprise an aqueous dispersion of water-insoluble emulsion vinyl addition polymer having an apparent  $T_g$  of from 5°C to 25°C, and water-insoluble core/shell particles of the present invention at a pigment volume concentration of at least about 5%, inorganic pigment, such as titanium dioxide, and optional extender.

In another embodiment the process of the present invention may be employed to encapsulate organic target materials such as organic compounds, which are relatively insoluble in water but soluble in the blend of solvent and monomer used to prepare the core emulsion. The material to be encapsulated is included in the mixture used in preparing the core emulsion. Examples of organic target materials which may be encapsulated by the process of the present invention include pesticides, biocides, herbicides, fungicides, insecticides, dyes, inks, colorants, chelating agents, perfumants, and pharmaceuticals. Any liquid or solvent-soluble solid, which is sufficiently hydrophobic, so that when mixed with aqueous dispersion of core emulsion it tends to become substantially distributed within the core emulsion phase, and does not inhibit polymerization of the core emulsion, may be microencapsulated by the present technique. Aqueous dispersions of microencapsulated pesticides, biocides, herbicides, fungicides, insecticides, and pharmaceuticals are especially useful in preparing controlled release formulations, in which the encapsulated material is slowly released from the microcapsule, as by diffusion through the microcapsule walls. Aqueous dispersions of microencapsulated pesticides, biocides, herbicides, fungicides, insecticides and the like may be included with other agricultural chemicals such as emulsifiable concentrates of pesticides in tank mixes and sprayed using conventional application equipment. Microencapsulation may result in reduced toxicity and extended effective application lifetime for pesticides and other toxic materials.

Examples of organic target compounds with biocidal activity include water-insoluble herbicidal diphenyl ethers such as oxyfluorfen and water-insoluble isothiazolone biocides such as 2-n-octyl-3-isothiazolone.

When employed to encapsulate inks, dyes and colorants and the like, the core/shell particles of the present invention may be released by application of mechanical force to the core/shell particles, or which otherwise breaks, melts, dissolves or otherwise destroys the integrity of the microcapsule shell. Alternatively, the shell of the core/shell polymer shell may be permeable to the target organic compound, resulting in slow continuous release of the target material from the core/shell particles.

Core/shell particles of the present invention encapsulating target organic materials such as biocides may be used to prepare microbe resistant coatings compositions, and especially water-based coatings compositions. For example, biocide encapsulated in an aqueous dispersion of water-insoluble core/shell articles of the present invention may be mixed with pigments, extenders, and vinyl addition latex polymer to form a coating composition. Core/shell particles may be prepared which both contribute opacity to the film formed by the coating composition in which they are included and slowly release biocidally active material to help preserve the coating film from microbial attack.

When employed to encapsulated target materials, it is preferred that ratio of solvent to initial monomer used to prepare the core/shell particles be 1:2.7.

In preparing microencapsulated target materials, a single stage process which does not employ additional monomer is preferred.

Core/shell particles of the present invention may also be prepared in the presence of an organic hydrophobic target material containing chemically reactive functional groups such as isocyanate functional groups and epoxy groups.

The core/shell particles may find use as or in coating, herbicidal or biocidal compositions.

The following abbreviations are used in the examples below:

EA	ethyl acrylate
MMA	methyl methacrylate
AN	acrylonitrile
MAA	methacrylic acid
S	styrene
BA	butyl acrylate
ALMA	allyl methacrylate

The following examples are illustrative of the present invention which is in no way limited thereby. In the examples the parts and percentages are by weight and temperatures are in degrees Celsius unless otherwise stated.

#### Example 1 - Preparation of Core/Shell Particles

A core emulsion is prepared by adding, to 200 parts of water, 100 parts of a solvent mixture composed of 70 parts Isopar G isoparaffin hydrocarbons (Isopar is a trademark of Exxon) and 30 parts n-pentanol, 100 parts of the initial (first stage) monomer mixture (5 parts ethyl acrylate, 92.5 parts methyl methacrylate, and 2.5 parts methacrylic acid), 6 parts of dioctylphthalate, 0.85 parts Monowet MO-70E surfactant (Monowet is a trademark of Mono Industries, Inc.) and 3.5 parts Alperox F lauryl peroxide (Alperox is a trademark of Pennwalt). The mixture is then emulsified at high shear (18,000 rpm) using a Micro-Mixer emulsifier, (manufactured by Charles Ross & Son Company, Hauppauge, N.Y.) for 7-10 minutes. 300 parts of core emulsion is mixed with 75 parts of water at room temperature in a 4-neck-round bottom flask equipped with a stirrer, thermometer and temperature regulator, condenser, and nitrogen stream. Under nitrogen, the temperature of the reaction mixture is raised to 85-87°C and this temperature is maintained for ½ hour. 6.5 parts of ammonia (5.6%) is then added through one of the necks and the reaction mixture is stirred for ½ hour. Gradual addition of the additional (second stage) monomer mixture is then begun. The second stage monomer mixture, contains 10 parts butyl acrylate, 87 parts methyl methacrylate and 2 parts allyl methacrylate. 73 parts of this mixture are gradually added over a 90-100 minute period to the reaction flask containing the initial core/shell particles. One-half hour after initiating the second stage monomer feed, 2.2 parts of dilute ammonia (5.6%) are added to the reaction flask. One hour after the second stage monomer feed is initiated another 2.2 parts of dilute ammonia (5.6%) is added. After the second stage monomer mixture feed has been completed, the temperature of the reaction flask is maintained for ½ hour. The reaction mixture is then cooled and decanted from the reaction flask.

#### Preparation of Polymer Film and Measurement of Opacity



An aqueous dispersion of core/shell particles is mixed with a commercially available film-forming acrylic latex polymer, RHOPLEX AC-64 polymer (RHOPLEX is a trademark of Rohm and Haas Company), in a 15-85 ratio (based on the weight of solids of each polymeric dispersion). The mixture of core/shell particles and film-forming latex polymer particles is diluted to a final total solids of 40%. A film is drawn down over black polyvinyl chloride sheets having a matte finish using an applicator having a 5 mil (0.0127 cm) aperture to give a nominal film thickness of 5 mils (0.0127 cm). Two draw downs are made, one for drying under low relative humidity (approx. 30%), the other under high humidity (about 70%). The two films are dried overnight. Light scattering from the dried films is then measured using a Gardner Colorgard 45% Reflectometer (Gardner Laboratories, Inc.). Kubelka-Munk scattering coefficients (s/ml) are calculated for the dried films by the method of P. B. Mitton and A. E. Jacobsen, Official Digest, Vol. 35, Federation of Paint and Varnish Production Clubs, ODFPA, Sept. 1963, pp 871-911.

Using the method of Example 1 above, aqueous dispersions of core/shell particles were prepared and their ability to opacify a model film was measured as described above.

Table I reports the results of varying the monomer composition of the first stage on the film opacity for core/shell particles prepared using the process of Example 1.

**TABLE I**  
Effect of First Stage Monomer Composition on  
Film Opacity

Example	First Stage <sup>2</sup> Composition	Film Opacity	
		S/ml	% Collapse
1	5 EA/92.5 MMA/2.5 MAA	.439	3
2	10 BA/87.5 MMA/2.5 MAA	.336	34
3	10 EA/87.5 MMA/2.5 MAA	.397	31
4	97.5 MMA/2.5 MAA	.371	21
5	5 AN/92.5 MMA/2.5 MAA	.362	17
6	5 S/92.5 MMA/2.5 MAA	.400	19

1. The process used employs solvent (hydrophobic plus hydrophilic), initial monomer (first stage), and additional monomer (second stage) in a weight ratio of 1:1:1. The solvent is a mixture of Isopar G isoparaffins and n-pentanol in a weight ratio of 7:3. 0.3% Monowet MO-70E surfactant (based on the weight of the organic phase in the initial stage) is employed.

2. Second stage monomer composition is 10 BA/88 MMA/2.0 ALMA.

3. The % collapse is determined as follows:

$$\frac{(S/mil)_{30\%} - (S/mil)_{70\%}}{(S/mil)_{30\%}}$$

The data in Table II give the effect of varying the composition of the second stage of the core/shell particles on film opacification.

TABLE II  
Effect of Second Stage Monomer Composition on Film Opacity

Example	Monomer Composition <sup>1</sup>		S/mil	% Collapse <sup>2</sup>
	Stage I	Stage II		
2	10 BA/87.5 MMA/2.5 MAA	10 BA/88 MAA/2 ALMA	.336	34
7	5 S/92.5 MMA/2.5 MAA	10 BA/88 MMA/2 ALMA	.400	19
8	5 S/92.5 MMA/2.5 MAA	10 EA/88 MMA/2 ALMA	.382	14
9	5 S/92.5 MMA/2.5 MAA	5 S/93 MMA/2 ALMA	.409	9
10	5 EA/92.5 MMA/2.5 MAA	5 S/93 MMA/2 ALMA	.349	10

1. The process used employs solvent (hydrophobic plus hydrophobic), initial monomer (first stage), and additional monomer (second stage) in a weight ratio of 1:1:1. The solvent is a mixture of Isopar G isoparaffins and n-pentanol in a weight ratio of 7:3. 0.3% Monowet MO-70E surfactant (based on the weight of the organic phase in the initial stage is employed).

2. The % collapse is determined as follows:  $\frac{(S/mil)_{30\%} - (S/mil)_{70\%}}{(S/mil)_{30\%}}$

Table III gives the effect of varying the solvent blend on the properties of core/shell particles prepared by the process of Example 1.

TABLE III  
Effect of Hydrophobic Solvent on Film Opacity<sup>1</sup>

Example	Solvent Properties				Film Properties <sup>7</sup>	
	Solvent	50% Dist. Temp.	Composition (%)		S/mil	% Collapse
			Paraf	Cyclo- paraf.		
11	Odorless Mineral Spirits	183	86	14	.222	32
12	Mineral Spirits 66/3	172	48	51	.219	14
13	Isopar G <sup>3</sup>	163	93	7	.249	10
14	Isopar H <sup>3</sup>	181	94	7	.217	31
15	Norpar 12 <sup>4</sup>	200	98	2	.268	41
16	Varsol <sup>5</sup>	172	46	40	.169	34
17	VM&P Naphtha <sup>6</sup>	122	49	41	.028	---

1. The process used to prepare the aqueous dispersions of core/shell particles employs solvent, initial monomer and additional monomer in a weight ratio of 1:1.3:1. The solvent is a mixture of n-pentanol and hydrophobic solvent in a weight ratio of 3:7. The monomer composition of Example 1 is used in preparing the core/shell particles.
  2. "Mineral spirits 66/3" refers to Amsco Mineral Spirits 66/3; from Union Chem. Div. of Union Oil Company.
  3. Isopar is a trademark of Exxon.
  4. Norpar is a trademark of Exxon, Norpar 12 solvent is a mixture of highly pure normal paraffins, and has 13% by weight C-10, 36% C-11, 44% C-12, and 7% C-13 alkanes.
  5. Varsol is a trademark of Exxon.
  6. VM&P naphtha is a narrow boiling fraction of petroleum.
  7. See footnote 2 of Table II.
- Table IV gives the effect of varying the methacrylate acid level in the first stage on the film opacification for core/shell particles prepared using the process of Example 1.



TABLE IV  
Effect of Methacrylic Acid Level on  
Film Opacity

<u>Example</u>	<u>% MAA<sup>1</sup></u>	<u>S/Mil</u>	<u>% Collapse<sup>2</sup></u> <u>(high % RH)</u>
18	2.0	.02	41
19	2.5	.22	32
19A		.25	7
20	3.0	.20	35
21	3.5	.02	73

1. The process used to prepare aqueous dispersion of core/shell particles employs solvent, initial monomer and additional monomer in a weight ratio of 1:1.3:1. A solvent blend of odorless mineral spirits and n-pentanol in a weight ratio of 7:3 is used. Example 18 has an initial monomer composition of 10 BA/88 MMA/2 MAA and an additional monomer composition of 10 BA/88 MAA/2 ALMA. In the succeeding examples, as the level of MAA is increased, the level of MMA is correspondingly decreased.

2. The % collapse is determined as follows:

$$\frac{(S/mil)_{30\%} - (S/mil)_{70\%}}{(S/mil)_{30\%}}$$

Table V gives the effect of varying the allyl methacrylate level in the second stage composition on the film opacification of core/shell particles prepared according to the process of Example 1.

TABLE V  
Effect of ALMA Level on Film Opacity

<u>Example</u>	<u>% ALMA<sup>1</sup></u>	<u>S/Mil</u>	<u>% Collapse<sup>2</sup></u>
22	0	.201	27
23	0.5	.213	18
24	1	.235	22
25	2	.247	7
26	3	.192	32
27	4	.212	29

1. The process used to prepare aqueous dispersions of core shell particles employs solvent, initial monomer and additional monomer in a weight ratio of 1:1.3:1. A solvent blend of colorless mineral spirits and n-pentanol in a weight ratio of 7:3 is used. Example 22 has an initial monomer composition of 10 BA/87.5 MMA/2.5 MAA and an additional monomer composition of 10 BA/90 MMA. In the succeeding examples, as the level of ALMA is increased, the level of MMA is correspondingly decreased.
2. The % Collapse and Calculated Shell Thickness and Void Volume are determined as for Examples 18-21 above.

Table VI gives the effect of varying the level of surfactant employed in the process of Example 1 on the film opacification of the core/shell particles produced.

TABLE VI  
Effect of Surfactant Level on Film Opacity

Example	% Surfactant/Org. Phase	S/Mil	% Collapse (high %RH)
28	0.3	.243	35
29	0.4	.264	19
30	0.5	.290	33
31	0.65	.244	24
32	0.8	.222	32
32a		.247	7

1. The process used to prepare aqueous dispersion of core/shell particles employs solvent, initial monomer and additional monomer in a weight ratio of 1:1.3:1. A solvent blend of odorless mineral spirits and n-pentanol in a weight ratio of 7:3 is used. The monomer composition is the same as Example 2 above. Example 28 is prepared using 0.3% Monowet MO-70E surfactant as a weight percentage of the organic phase in the initial polymerization stage.
2. The % Collapse, is determined as for Examples 18-21 above.

#### Example A - Encapsulation of Methyl Hexanoate

A core emulsion is prepared by adding, to 233 parts of water, 100 parts of a solvent mixture (55 parts Isopar G isoparaffins/30 parts n-pentanol/15 parts methyl hexanoate), 133 parts of monomer mixture (97.5 parts methyl methacrylate/2.5 parts methacrylic acid), 7 parts dioctyl phthalate, 1 part of Monowet-70E surfactant, and 4.7 parts of Alperoxide-F lauryl peroxide initiator. The mixture is then emulsified by mixing at high shear (18,000 rpm) for 10 minutes using a Ross Micro-Mixer Emulsifier. 250 parts of the core emulsion is transferred to a reaction vessel consisting of a 4-neck round-bottom flask equipped with a stirrer, thermometer and temperature regulator, condenser and a nitrogen stream. 62.5 parts of water is added to the reaction flask. Under nitrogen the temperature of the reaction mixture is brought to 85-88°C and maintained at that temperature for ½ hour. 6.2 parts of diluted ammonia (5.6%) is then added and the temperature is maintained for another ½ hour. Gradual addition of additional (second stage) monomer mixture is then begun. The monomer mixture consists of 52.2 parts of a mixture of 98 parts methyl methacrylate to 2 parts of allyl methacrylate. The second stage mixture is added over a period of

approximately 75 minutes. Approximately 25 minutes after beginning the gradual addition of second stage monomer, 2.1 parts of dilute ammonia (5.6%) is added. Approximately 50 minutes after initiating the gradual addition of second stage monomer another 2.1 parts of dilute ammonia (5.6%) is added. The temperature of the reaction flask is maintained for 30 minutes after completion of the second stage monomer feed after which the reaction flask is cooled and the aqueous dispersion of core/shell particles is decanted. The core/shell particles of this preparation give a film opacity of 0.28 s/mil. The hydrolysis rate of the encapsulated methyl hexanoate was measured at a pH of 11.5 using gas liquid chromatography. The half life of the encapsulated ester was 83 minutes in comparison with the half life of 17 minutes for unencapsulated ester.

10

#### Example B - Encapsulation of SKANE Biocide

A core emulsion is prepared by adding to 367 parts of water 100 parts of a solid mixture composed of 55 parts odorless mineral spirits, 30 parts n-pentanol and 15 parts SKANE M-8 (SKANE is a trademark of Rohm and Haas Company) biocide. 268 parts of a monomer mixture composed of 10 parts butyl acrylate, 88.5 parts methyl methacrylate and 2.5 parts methacrylic acid are added, as are 11 parts dioctyl phthalate, 2.6 parts Monowet MO-70E surfactant, and 9.3 parts lauroyl peroxide initiator. The mixture is then emulsified at high speed (18,000 rpm) using a Ross Micro-Mixer Emulsifier for 10 minutes. 250 parts of the core emulsion is transferred to a reaction vessel as in Example 1. 62.5 parts of water is added to the reaction vessel. Under nitrogen the temperature of the reaction mixture is brought to 85-88°C and the temperature is maintained for 60 minutes. 7.8 parts of dilute ammonia (5.6%) are then added and the temperature is maintained at 85-88°C for an additional 30 minutes. The reaction mixture is then cooled and decanted. Example B is repeated except that a solvent mixture of 40 parts odorless mineral spirits, 30 parts n-pentanol and 30 parts SKANE biocide is employed yielding Example B-1.

25 Aqueous latex paint is prepared according to the following formulation:

	<u>Materials</u>	<u>Parts by Weight</u>
30	water	58
	methyl carbitol	59
	QR-681M dispersant	7.1
	TRITON N-57 surfactant	4.0
35	Colloid 643 defoamer	1.0
	TiPure R-902 titanium dioxide	225
	Minex 4 pigment	160
40	Icecap K pigment	50

45 The above ingredients are ground at high speed (3800-4500 rpm) for 10-15 minutes and the let down at slower speed with the following additional ingredients:

50

55



	water	50
	Rhoplex AC-64 polymer emulsion	306
5	Colloid 643 defoamer	3.0
	Texanol coalescent	9.0
	NH <sub>4</sub> OH	2.9
10	Natrosol 250 MHR thickener	199.6
	water	22.1
	<u>Formulation Constants</u>	
15	Initial viscosity, KU	88
	pH	9.5

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20

QR-681M is a dispersant and a product of Rohm and Haas Company.

25

TRITON N-57 surfactant is a product of Rohm and Haas Company. CAS Registry No. 9016-45-9.

30

Colloid 643 is an antifoam agent and a product of Colloids, Inc.

TiPure R-902 titanium dioxide is a product of E. I. DuPont De Nemours Co.

35

Minex 4 clay is a product of Indusmin Co.

Icecap K is a product of Burgess Pigment Co.

40

RHOPLEX AC-64 polymer latex emulsion is a product of Rohm and Haas Company.

Natrosol 250 MHR cellulosic thickener is a product of Hercules, Inc.

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45

This paint was spiked with encapsulated biocide of Example B to provide a test paint with 2 grams of active ingredient/1200 gms of paint.

50

Table VII gives the result of encapsulating the biocide on its heat-age stability in paints. The heat-aged stability is measured by placing the test paint in a 60° C oven for aging. At appropriate intervals samples are taken and analyzed for SHAKE M-8 biocide via a GLC technique.

55

TABLE VII									
% of Initial Skane M-8 Biocide Remaining									
First Series					Second Series				
Days at 60°C	Uncapsu- lated Biocide	Encapsu- lated 15%	Days at 60°C	Unencap- sulated Biocide	Encapsu- lated 15%	Encapsu- lated 30%			
0	100	100	0	100	100	100			
4	81.5	100	5	32	100	100			
7	0	100	9	0	100	100			
10	-	99	12		100	100			
13		100			100	100			
16		99	16		100	52			
20		99	20		100	0			
24		84			100	100			
27		91	26		100	100			
			30		100	100			
31		76			100	100			
			35		100	100			
			40		100	100			
			44		100	100			
			51		45				
1. % SKANE M-8 biocide on solvent core.									

The results in Table VII indicate that encapsulation of the biocide by the process of present invention increases the heat-age stability of the biocide in paint compositions. Heat-age stability is believed to be predictive of long-term room temperature storage stability of paint formulations.

#### Example C - Encapsulation of GOAL Herbicide

A core emulsion is prepared by adding to 368 parts of water 100 parts of solvent mixture consisting of 45 parts Isopar G, isoparaffins, 30 parts n-pentanol and 25 parts technical grade GOAL oxyfluorfen herbicide (GOAL is a trademark of Rohm and Haas Company). 270 parts of a monomer mixture (5 parts ethyl

acrylate/92.5 parts methyl methacrylate/2.5 parts methacrylic acid) is added to the core emulsion mixture as are 11 parts dioctyl phthalate, 2.5 parts Monowet MO-70E surfactant, and 9.4 parts Alperoxide F lauryl peroxide initiator. The mixture is then emulsified at high shear, (18,000 rpm) for about 7 to 10 minutes using a Ross Micro-Mixer Emulsifier.

5 250 parts of the core emulsion are transferred to the reaction vessel of Example 1 and 24.2 parts of water is added. Under nitrogen the temperature of the reaction mixture is brought to 85-88° C and there maintained for 60 minutes. Subsequently 7.8 parts of dilute ammonia (5.6%) is added to the reaction mixture and the temperature is maintained for another 30 minutes after which the reaction mixture is cooled and decanted to give Example C-1.

10 The same procedure is repeated substituting 50 parts by weight and 70 parts by weight of GOAL herbicide to yield Examples C-2 and C-3 respectively.

The procedure of Example C is repeated substituting (15% by weight on Isopar G/n-pentanol core solvent) a haloketone herbicide disclosed in U.S. Patent 3,661,991, namely N-(1-methyl-1-ethyl-3-chloroacetyl)-3,5-dichlorobenzamide, yielding Example D.

15 The procedure of Example C is repeated substituting (15% by weight on Isopar G/n-pentanol core solvent) a triazole fungicide, namely, alpha-(4-chlorophenyl)-butyl-1H-1,2,4-triazole-propane-nitrile yielding Example E.

The following are trade marks which may or may not be registered in one or all of the designated states:

20

	ISOPAR	WARING	TiPURE
	MONOWET	NORPAR	MINEX
25	ALPEROX	VAR SOL	ICE CAP
	ROSS MICRO-MIXER	ALPEROXIDE	TEXANOL
	RHOPLEX	SKANE	NATROSOL
30	GARDNER COLORGARD	TRITON	GOAL
	AMSCO	COLLOID	

### 35 Claims

1. A process for preparing an aqueous dispersion of water-insoluble core/shell particles comprising
  - (a) preparing core emulsion by emulsifying in water at high shear a mixture comprising
    - (1) at least one hydrophobic solvent and/or organic target material,
    - (2) at least one hydrophilic solvent,
    - (3) initial monomer comprising at least two polymerizable mono-ethylenically unsaturated compounds wherein said initial monomer includes from 2 to 4 percent by weight, based on total weight of said initial monomer, of alpha, beta-ethylenically unsaturated carboxylic acid monomer,
    - (4) anionic surfactant,
    - (5) water-insoluble emulsion stabilizer, and
    - (6) water-insoluble thermal polymerization initiator, wherein said hydrophobic solvent and said hydrophilic solvent are non-solvents for polymer prepared by polymerizing said initial monomer,
  - (b) heating said core emulsion to polymerize said initial monomer, thereby forming core particles,
  - (c) adding at least one base selected from ammonia and the organic amines thereby neutralizing polymerized carboxylic acid and forming core/shell particles, and optionally
  - (d) adding additional monomer whereby said additional monomer is polymerized on or in the previously formed shell of said core/shell particles.
2. A process as claimed in claim 1 wherein additional polymerization initiator is added subsequent to neutralization of core particle polymerized carboxylic acid.
3. A process as claimed in claim 1 or claim 2, wherein the weight ratio of components 1 and 2 : component 3 of the core emulsion is from 1:0.8 to 1:3.

4. A process as claimed in any one of the preceding claims, wherein said hydrophobic solvent has a 50% distillation temperature of from 150 ° C to 200 ° C, preferably from 160 ° C to 180 ° C.
5. A process as claimed in any one of the preceding claims wherein the hydrophobic solvent is selected from the acyclic paraffinic hydrocarbons, mixtures of the acyclic paraffinic hydrocarbons and cyclic paraffinic hydrocarbons, and mixtures of acyclic paraffinic hydrocarbons, cyclic paraffinic hydrocarbons and aromatic hydrocarbons wherein said mixtures contain no more than 10% by weight, based on the total weight of the mixture, of aromatic hydrocarbon.
6. A process as claimed in any one of the preceding claims, wherein the hydrophilic solvent is a hydroxyl compound and wherein there are from 0.28 to a 0.42 moles of hydroxyl functional groups per 100 g. of the total weight of hydrophilic and hydrophobic solvent.
7. A process as claimed in any one of claims 1 to 5 wherein the weight ratio of the hydrophilic solvent to hydrophobic solvent is from about 1:3 to about 9:11.
8. A process as claimed in any one of the preceding claims wherein the hydrophilic solvent is selected from the isomers of butanol, pentanol, hexanol, and methyl isobutyl carbinol, and mixtures thereof.
9. A process as claimed in any one of the preceding claims, wherein said initial monomer is selected to yield polymer having a calculated glass transition temperature at least 70 ° C.
10. A process as claimed in any one of the preceding claims wherein said aqueous dispersion is at least partially dried to yield particles which contain single voids and cause opacity in compositions in which they are contained.
11. A process as claimed in any one of the preceding claims wherein the target organic compound has biocidal or herbicidal activity and is preferably selected from 2-n-octyl-3-isothiazolone, oxyfluorfen and mixtures thereof.
12. A process as claimed in any one of claims 1 to 10 wherein the organic target compound contains at least one chemically reactive functional group, preferably selected from isocyanate functional group or epoxy group.
13. Use of a composition comprising core/shell particles prepared by the process as claimed in any one of the preceding claims as or in a coating composition, a herbicidal composition or a biocidal composition.

#### Revendications

1. Procédé de préparation d'une dispersion aqueuse de particules insolubles dans l'eau, comportant un cœur et une gaine, consistant :
  - (a) à préparer une émulsion de cœur par émulsification dans l'eau, à cisaillement élevé, d'un mélange comprenant :
    - (1) au moins un solvant hydrophobe et/ou un matériau cible organique,
    - (2) au moins un solvant hydrophile,
    - (3) un monomère initial comprenant au moins deux composés polymérisables à insaturation monoéthylénique, ledit monomère initial contenant de 2 à 4 % en poids, par rapport au poids total dudit monomère initial, d'un acide carboxylique à insaturation alpha,bêta-éthylénique, monomère,
    - (4) un tensioactif anionique,
    - (5) un stabilisant d'émulsion insoluble dans l'eau, et
    - (6) un amorceur de polymérisation thermique insoluble dans l'eau, ledit solvant hydrophobe et ledit solvant hydrophile étant des non-solvants pour le polymère préparé par la polymérisation dudit monomère initial,
  - (b) à chauffer ladite émulsion de cœur pour polymériser ledit monomère initial de façon à former des particules de cœur,
  - (c) à ajouter au moins une base, choisie parmi l'ammoniac et les amines organiques, de façon à neutraliser l'acide carboxylique polymérisée et à former des particules cœur/gaine, et facultative-



ment

(d) à ajouter du monomère supplémentaire de façon que ledit monomère supplémentaire soit polymérisé sur ou dans la gaine préalablement formée desdites particules cœur/gaine.

- 5 2. Procédé selon la revendication 1, dans lequel de l'amorceur de polymérisation supplémentaire est ajouté après la neutralisation de l'acide carboxylique polymérisé des particules de cœur.
3. Procédé selon la revendication 1 ou 2, dans lequel le rapport pondéral entre les composants 1 et 2 et le composant 3 de l'émulsion de cœur est de 1:0,8 à 1:3.
- 10 4. Procédé selon l'une quelconque des revendications précédentes, dans lequel ledit solvant hydrophobe a une température de distillation à 50 % de 150 à 200, de préférence de 160 à 180 °C.
- 15 5. Procédé selon l'une quelconque des revendications précédentes, dans lequel le solvant hydrophobe est choisi parmi les hydrocarbures paraffiniques acycliques, les mélanges des hydrocarbures paraffiniques acycliques et d'hydrocarbures paraffiniques cycliques, et les mélanges d'hydrocarbures paraffiniques acycliques, d'hydrocarbures paraffiniques cycliques et d'hydrocarbures aromatiques, lesdits mélanges ne contenant pas plus de 10 % en poids, par rapport au poids total du mélange, d'hydrocarbure aromatique.
- 20 6. Procédé selon l'une quelconque des revendications précédentes, dans lequel le solvant hydrophile est un composé hydroxylé, et dans lequel on a 0,28 à 0,42 mole de groupes à fonctionnalité hydroxyle par 100 g de poids total de solvant hydrophile et hydrophobe.
- 25 7. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel le rapport pondéral du solvant hydrophile au solvant hydrophobe est d'environ 1:3 à environ 9:11.
8. Procédé selon l'une quelconque des revendications précédentes, dans lequel le solvant hydrophile est choisi parmi les isomères du butanol, du pentanol, de l'hexanol et du méthylisobutylcarbinol, et leurs mélanges.
- 30 9. Procédé selon l'une quelconque des revendications précédentes, dans lequel ledit monomère initial est choisi de façon à donner un polymère ayant une température calculée de transition vitreuse d'au moins 70 °C.
- 35 10. Procédé selon l'une quelconque des revendications précédentes, dans lequel ladite dispersion aqueuse est au moins partiellement séchée, pour donner des particules contenant des cavités individuelles et provoquer l'opacité des compositions dans lesquelles elles sont contenues.
- 40 11. Procédé selon l'une quelconque des revendications précédentes, dans lequel le composé organique cible a une activité biocide ou herbicide et est de préférence choisi parmi la 2-n-octyl-3-isothiazolone, l'oxyfluorène et leurs mélanges.
- 45 12. Procédé selon l'une quelconque des revendications 1 à 10, dans lequel le composé organique cible contient au moins un groupe fonctionnel chimiquement réactif, de préférence choisi parmi les groupes à fonctionnalité isocyanate ou les groupes époxydes.
- 50 13. Utilisation d'une composition comportant des particules cœur/gaine, préparée par le procédé selon l'une quelconque des revendications précédentes, sous forme ou au sein d'une composition de revêtement, d'une composition herbicide ou d'une composition biocide.

#### Patentansprüche

1. Verfahren zur Herstellung einer wäßrigen Dispersion von wasserunlöslichen Kern-/Hüll-Teilchen, bei dem man
  - 55 (a) eine Kern-Emulsion herstellt, indem in Wasser bei großer Scherung ein Gemisch emulgiert wird, umfassend
    - (1) mindestens ein hydrophobes Lösungsmittel und/oder organisches Zielmaterial,

- (2) mindestens ein hydrophiles Lösungsmittel,  
 (3) ein Ausgangsmonomer, das mindestens zwei polymerisierbare mono-ethylenisch ungesättigte Verbindungen enthält, worin das Ausgangsmonomer 2 bis 4 Gew.-%, basierend auf dem Gesamtgewicht des Ausgangsmonomers, eines alpha-beta-ethylenisch ungesättigten Carbonsäure-Monomer einschließt,  
 (4) ein anionisches Tensid,  
 (5) einen wasserunlöslichen Emulsions-Stabilisator, und  
 (6) einen wasserunlöslichen thermischen Polymerisations-Initiator, worin das hydrophobe Lösungsmittel und das hydrophile Lösungsmittel keine Lösungsmittel für das durch Polymerisierung des Ausgangsmonomers hergestellten Polymers sind,  
 (b) die Kern-Emulsion zur Polymerisierung des Ausgangsmonomers erhitzt, um Kern-Teilchen auszubilden,  
 (c) mindestens eine Base zugibt, die aus Ammoniak und den organischen Aminen ausgewählt ist, um die polymerisierte Carbonsäure zu neutralisieren und Kern-/Hüll-Teilchen auszubilden, und gegebenenfalls  
 (d) ein zusätzliches Monomer zugibt, wodurch das zusätzliche Monomer auf oder in der vorher ausgebildeten Hülle der Kern-/Hüll-Teilchen polymerisiert wird.
2. Verfahren nach Anspruch 1, worin ein weiterer Polymerisations-Initiator nach Neutralisierung eines Kern-Teilchens von polymerisierter Carbonsäure zugegeben wird.
3. Verfahren nach Anspruch 1 oder 2, worin das Gewichtsverhältnis der Komponenten 1 und 2 zu Komponente 3 der Kern-Emulsion 1:0,8 bis 1:3 beträgt.
4. Verfahren nach einem der vorhergehenden Ansprüche, worin das hydrophobe Lösungsmittel eine 50 %-Destillations-Temperatur von 150 °C bis 200 °C, vorzugsweise 160 °C bis 180 °C hat.
5. Verfahren nach einem der vorhergehenden Ansprüche, worin das hydrophobe Lösungsmittel aus den acyclischen Paraffin-Kohlenwasserstoffen, Gemischen der acyclischen Paraffin-Kohlenwasserstoffe und cyclischen Paraffin-Kohlenwasserstoffe und Gemischen acyclischer Paraffin-Kohlenwasserstoffe, cyclischer Paraffin-Kohlenwasserstoffe und aromatischer Kohlenwasserstoffe ausgewählt ist, worin die Gemische nicht mehr als 10 Gew.-%, basierend auf dem Gesamtgewicht des Gemisches, eines aromatischen Kohlenwasserstoffes enthalten.
6. Verfahren nach einem der vorhergehenden Ansprüche, worin das hydrophile Lösungsmittel eine Hydroxyl-Verbindung ist und worin 0,28 bis 0,42 Mol Hydroxyl-funktionelle Gruppen pro 100 g Gesamtgewicht hydrophilen und hydrophoben Lösungsmittels vorliegen.
7. Verfahren nach einem der Ansprüche 1 bis 5, worin das Gewichtsverhältnis des hydrophilen Lösungsmittels zum hydrophoben Lösungsmittel etwa 1:3 bis etwa 9:11 ist.
8. Verfahren nach einem der vorhergehenden Ansprüche, worin das hydrophile Lösungsmittel aus den Isomeren von Butanol, Pentanol, Hexanol und Methylisobutylcarbinol und Gemischen davon ausgewählt ist.
9. Verfahren nach einem der vorhergehenden Ansprüche, worin das Ausgangsmonomer so gewählt ist, daß ein Polymer mit einer berechneten Glas-Übergangstemperatur von mindestens 70 °C erhalten wird.
10. Verfahren nach einem der vorhergehenden Ansprüche, worin die wäßrige Dispersion mindestens teilweise getrocknet ist, um Teilchen zu erhalten, die einzelne Hohlräume enthalten und in sie enthaltenden Zusammensetzungen eine Lichtundurchlässigkeit verursachen.
11. Verfahren nach einem der vorhergehenden Ansprüche, worin die organische Zielverbindung Biozid- oder Herbizid-Aktivität hat und vorzugsweise aus 2-n-Octyl-3-isothiazolon, Oxyfluorfen und Gemischen davon ausgewählt ist.
12. Verfahren nach einem der Ansprüche 1 bis 10, worin die organische Zielverbindung mindestens eine chemisch reaktive funktionelle Gruppe enthält, die vorzugsweise aus Isocyanat-funktioneller Gruppe

oder Epoxygruppe, ausgewählt ist.

13. Verwendung einer Zusammensetzung, umfassend Kern-/Hüll-Teilchen, hergestellt durch das Verfahren  
der vorhergehenden Ansprüche oder in einer Beschichtungs-Zusammensetzung, Herbizid-Zusammen-  
setzung oder Biozid-Zusammensetzung.

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